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THRESHOLD ELECTRON STUDIES OF GAS-SURFACE INTERACTIONS
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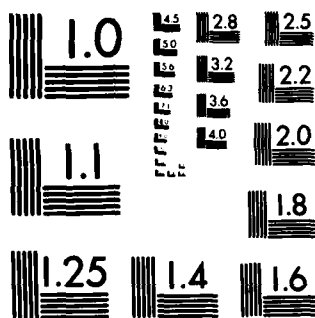
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THRESHOLD ELECTRON STUDIES OF GAS-SURFACE INTERACTIONS

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P. Terrance Murray

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300 College Park Avenue
Dayton, OH 45469

January 1985

Final Report for Period - 1 September 1983 to 31 October 1984

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20. threshold electron spectrometer which incorporated a steradiancy filter to selectively detect low energy electrons. The feasibility experiments entailed using a lithium fluoride thin films as the test specimen. The resulting threshold excitation spectrum exhibited peaks at 3.5, 4.5, and 6.3 eV; this was in excellent agreement with previous electron transmission studies in which the peaks were attributed to optically forbidden excitonic transitions at the lithium fluoride surface. The fact that similar structure was observed in this program (with better energy resolution) demonstrated that TES is indeed a feasible method of performing surface analysis.

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TABLE OF CONTENTS

SECTION		PAGE
I	ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS	1
II	INTRODUCTION	2
III	EXPERIMENTAL APPROACH	4
IV	SUMMARY OF RESEARCH	9
	1. EXPERIMENTAL APPROACH	9
	a. Apparatus Construction	9
	b. Data Acquisition	11
	c. Specimen Preparation	11
	2. EXPERIMENTAL RESULTS	12
	3. PRESENTATIONS AND PUBLICATIONS	12
V	REFERENCES	15

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SECTION I

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

↙ The purpose of this program was to test the feasibility of using threshold excitation spectroscopy (TES) as a new method of performing surface analysis. The TES experiments entailed bombarding the specimen of interest with a beam of nearly monoenergetic electrons and detecting those electrons which underwent near total energy loss upon colliding with the target surface. The result of such a collision was a scattered electron with a final kinetic energy close to zero. The program involved designing and constructing a threshold electron spectrometer which incorporated a steradiancy filter to selectively detect low energy electrons. The feasibility experiments entailed using lithium fluoride thin films as the test specimen. The resulting threshold excitation spectrum exhibited peaks at 3.5, 4.5, and 6.3 eV; this was in excellent agreement with previous electron transmission studies in which the peaks were attributed to optically forbidden excitonic transitions at the lithium fluoride surface. The fact that similar structure was observed in this program (with better energy resolution) demonstrated that TES is indeed a feasible method of performing surface analysis.

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SECTION II

INTRODUCTION

Electron energy loss spectroscopy (EELS) is a powerful technique for determining the excitation pathways⁽¹⁻³⁾ of solid surfaces as well as the vibrational modes^(4,5) of surface adsorbates. Such experiments entail bombarding the specimen of interest with a beam of nearly monoenergetic electrons and performing kinetic energy analysis on those electrons scattered from the surface. One characteristic of the conventional EELS experiment is the low efficiency with which the scattered electrons are collected; this is primarily a result of the small solid angle through which most dispersive analyzers, by necessity, must operate. One consequence of this fact is that a considerable electron dose may be required to achieve acceptable statistics in the loss spectrum. Such a large dose is significant in that it may lead to specimen damage by the probe beam. This is a particularly severe problem with the alkali halides, the alkaline earth halides, and a number of metal oxides⁽⁶⁾. A second consequence is that a significant time may be required to obtain the EELS information. This is not a serious concern for relatively unreactive specimens (such as the refractory metals), but other more reactive materials (such as the alkali metals) may react with background gases during a lengthy analysis. Reducing the data acquisition time would clearly help to extend the applicability of EELS to such reactive surfaces.

The solution to both problems lies in increasing the collection efficiency of the scattered electrons while maintaining good energy resolution. These requirements can be met by detecting those electrons which undergo near total energy loss and scatter with a final energy close to zero; these low energy electrons are formed at the threshold of a particular excitation channel and are thus designated threshold electrons. This approach was suggested by the University of Dayton in a proposal which was submitted to the Air Force Office of Scientific Research and

subsequently funded on a one-year basis in September 1983 (AFOSR-83-0260). During the past year, a threshold excitation spectrometer was designed, fabricated, and successfully operated, and the feasibility of using threshold excitation spectroscopy as a surface analysis tool was unambiguously demonstrated. A summary of the research program is presented in this final report.

SECTION III

EXPERIMENTAL APPROACH

The key to TES experiments is the ability to detect, and distinguish as such, low energy electrons scattered from the surface of interest. A number of approaches have been developed to detect low energy electrons in gas phase electron spectroscopy, and among these are the trapping technique of Schulz⁽⁷⁾, the field penetration method of Cvejano⁽⁸⁾, and the resonant attachment approach suggested by Curran⁽⁹⁾ and developed by other workers⁽¹⁰⁾. None of these elegant solutions is directly applicable to surface studies.

The method best suited for the TES experiments entails using a steradiance filter which was first proposed by Baer and co-workers in 1969⁽¹¹⁾. A schematic diagram of such a device is presented in Figure 1. A steradiance filter selectively transmits threshold electrons and spatially discriminates against those with higher energy. The filter consists of an acceleration region followed by a field-free drift tube. A threshold electron formed in the low field environment (approximately 1 volt/cm) of the former will be accelerated to a terminal velocity whose direction is parallel to the applied field. Such electrons are transmitted through the apertures of the drift tube and are detected by an electron multiplier. The trajectory of such a low energy electron is represented by path "a" in Figure 1. Energetic electrons, in general, have a velocity component normal to the field direction. These electrons hit the walls of the analyzer in the parabolic trajectories (denoted by path "b" in Figure 1) and are not detected. The energy resolution of a steradiance filter is a function of the initial electron energy (E_i), the energy gained by the electrons in the electric field (E_g), and the diameter-to-length ratio (d/l) of the drift region. Baer has derived an expression⁽¹¹⁾ for the steradiance function $F(E_i)$ which is given in Equation (1).

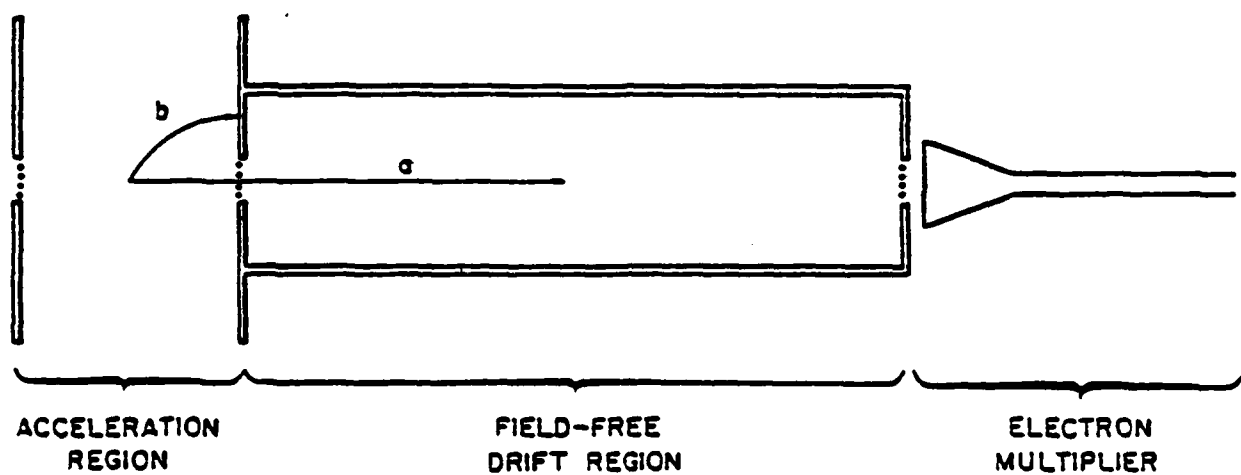


Figure 1. Schematic Diagram of a Steradiancy Filter.

$$F(E_i) = \begin{cases} 1 & ; E_i \leq E_g (\tan^2 \theta_c) \\ 1 - \left[1 - \left(\frac{E_g}{E_i} + 1 \right) \sin^2 \theta_c \right]^{1/2} & ; E_i \geq E_g (\tan^2 \theta_c) \end{cases}$$

In this expression

$F(E_i)$ the probability of detecting an electron with initial energy E_i
 θ_c critical angle defined as $\tan^{-1} \frac{d}{2\ell}$.

The steradiancy function is plotted in Figure 2 with experimentally reasonable values ($E_g = 2$ eV, $\theta_c = 2.6^\circ$). The full width at half maximum of approximately 6 meV makes this an extremely attractive technique for EELS studies. An additional desirable characteristic is the fact that threshold electrons can be detected with efficiencies near 50 percent⁽¹²⁾. Thus, the technique is potentially capable of providing EELS data with significantly less primary electron dose than the conventional approach.

One major drawback to the filter has traditionally been the high energy "tail" which never goes to zero (see Figure 2). This feature is due to energetic electrons whose initial velocity vectors are directed parallel to the electric field. Such high energy electrons will always be collected regardless of their energy. However, this detriment was overcome by the Principal Investigator and Baer in 1979.⁽¹³⁾ This was accomplished by taking advantage of the fact that energetic electrons arrived at the detector before the threshold electrons. That is, they have, a different time-of-flight (TOF). In that study⁽¹³⁾ a threshold electron spectrum was obtained by using a steradiancy filter in conjunction with TOF analysis of the electrons. The threshold electrons were formed by

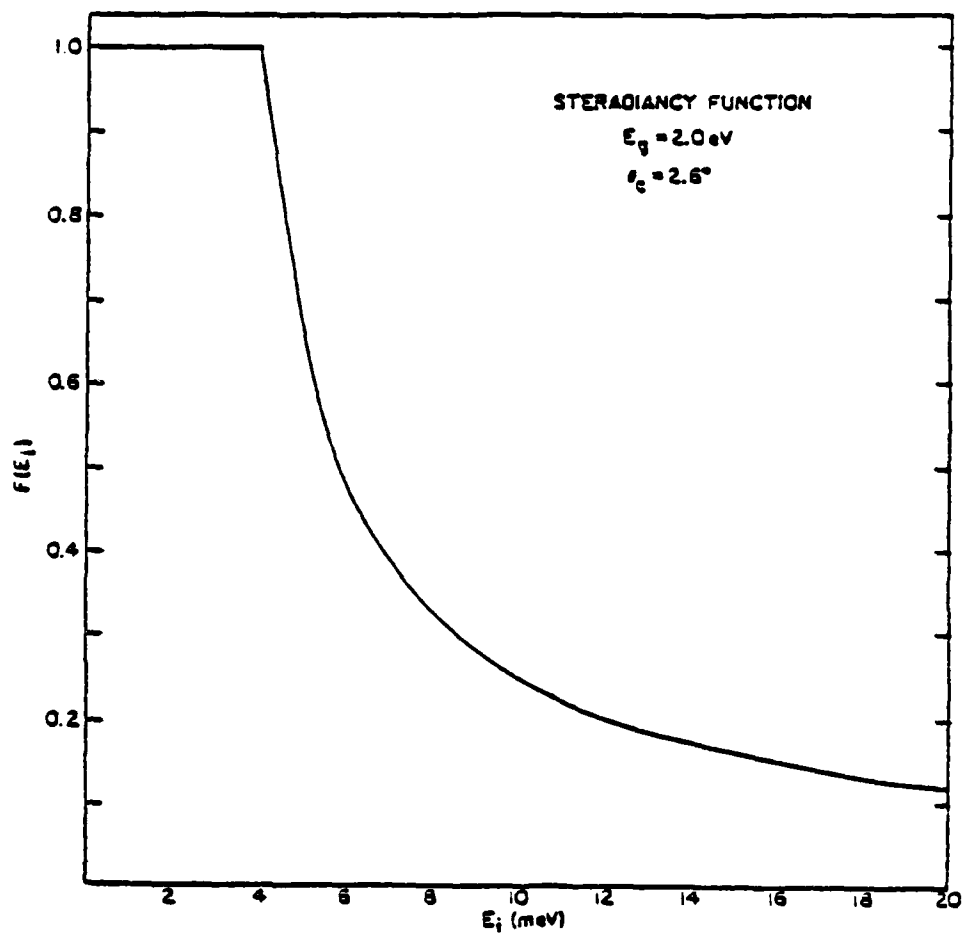


Figure 2. A Plot of the Steradiancy Function $F(E_i)$ versus the Initial Electron Energy E_i .

photoionization with a total energy resolution of 25 meV; however, 24 meV of this was due to the 2\AA band pass of the photon source. Thus a combination of spatial (steradiancy analyzer) and temporal (TOF analysis) discrimination provided extremely good energy resolution (near 1 meV). Such an analysis scheme is ideally suited to TES studies because of its excellent energy resolution, high collection efficiency, and simple geometry.

SECTION IV

SUMMARY OF RESEARCH

The University of Dayton proposed to test the feasibility of using TES as a means of performing surface analysis in a proposal which was submitted to AFOSR and subsequently funded on a one-year basis in September 1983. During the past year, a threshold excitation spectrometer was designed, fabricated, and successfully operated, and the feasibility of using TES as a surface analysis tool was unambiguously demonstrated. More details of the research program are presented below.

1. EXPERIMENTAL APPROACH

a. Apparatus Construction

The first phase of the program entailed designing and fabricating the apparatus shown schematically in Figure 3. The system consists of a commercial electron source (Apex Electronics, Paramus, New Jersey), a set of precision-machined hemispherical sectors, a set of focusing lenses, a specimen holder, a flight tube assembly, and a channel electron multiplier. These components (with the exception of the specimen holder) are mounted on a single 8-inch flange which mounts into an ultrahigh vacuum chamber. This arrangement provides reliable electrical connections, establishes a rigid experimental geometry, and allows the entire assembly to be removed from the vacuum chamber for repairs or modifications. All stainless steel components of the apparatus were hydrogen-annealed (Wall-Colmonoy, Dayton, Ohio) to remove residual magnetic fields, and the assembly is enclosed within one layer of mu metal shielding to attenuate any external magnetic fields (e.g., from ion pumps) inside the vacuum system. The vacuum chamber is pumped by a Varian ion pump and achieves a base pressure of 8×10^{-10} Torr after extensive baking.

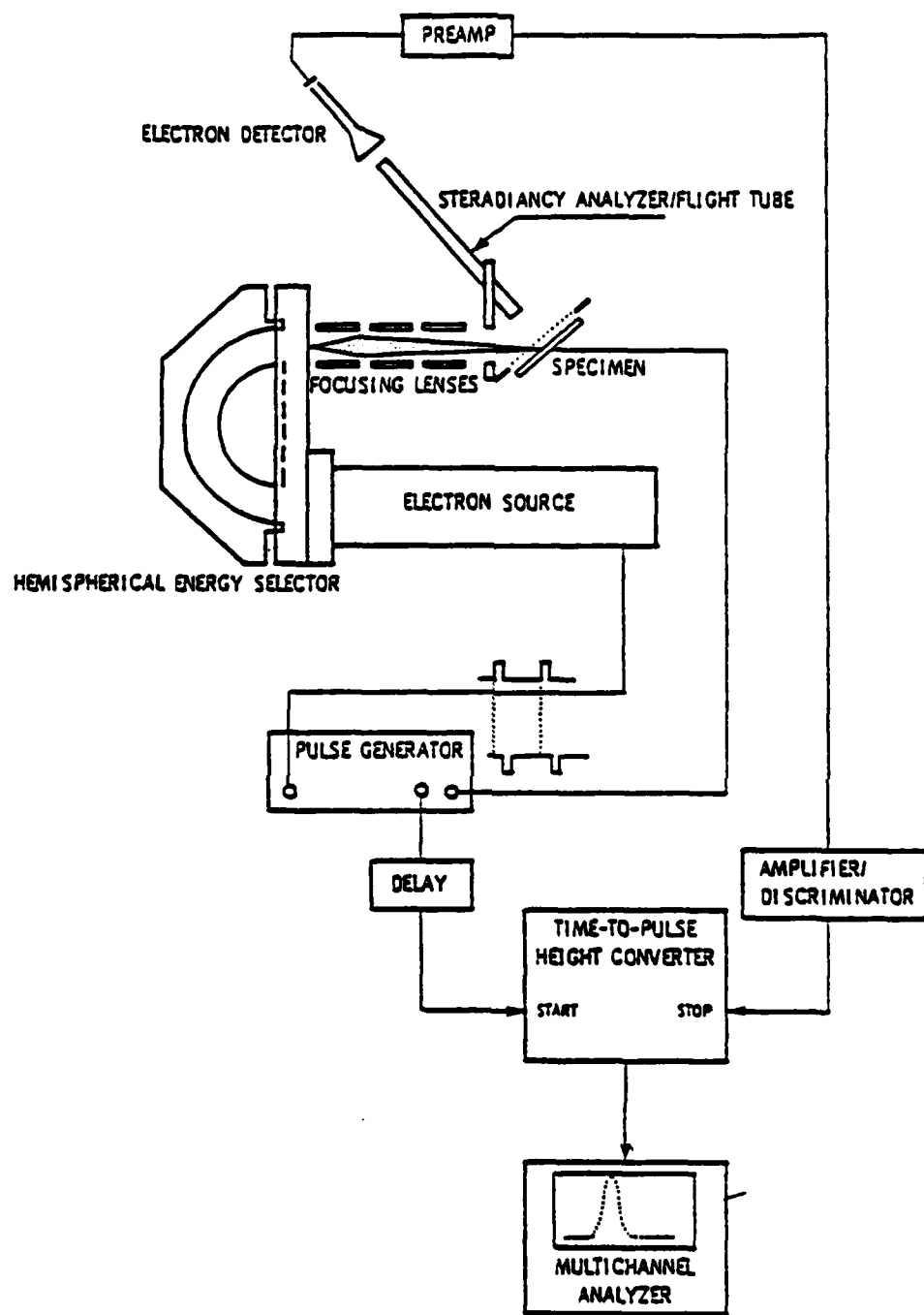


Figure 3. Schematic Representation of the Threshold Excitation Spectrometer.

b. Data Acquisition

Electrons are detected by a channel electron multiplier (Galileo 4800 series), the pulses from which are amplified by a preamplifier/discriminator (Ortec 9302). The signal from the latter is then handled in one of two ways. In the first, the signal is fed directly into a multichannel analyzer (Nuclear Data model ND62) operating in the multichannel scaling mode. The initial experiments were carried out in this fashion and consisted of scanning the channel address of the analyzer while ramping the initial energy of the electrons striking the specimen surface. The other mode of operation, which was used in the second phase of the program, entailed measuring the time-of-flight (TOF) distributions of the scattered low energy electrons. This was accomplished by applying a negative-going pulse to the specimen and measuring the electron TOF with a time-to-pulse height converter and multichannel pulse height analyzer as shown in Figure 3.

c. Specimen Preparation

The experiments carried out during the previous year focused on electron scattering from thin films (approximately 200Å) of LiF; such films have been examined by a number of other workers⁽¹⁴⁾. It was anticipated, therefore, that a comparison of the TES results with those obtained previously would be relatively straightforward.

The films were vapor-deposited onto a stainless steel substrate, the deposition being carried out within the ultrahigh vacuum chamber. These films were prepared in a manner suggested by Huang and Hamill⁽¹⁵⁾ which entailed resistively heating a LiF-coated wire which was located approximately 1 cm above the substrate. The TES experiments were initiated approximately five minutes after the films were prepared.

2. EXPERIMENTAL RESULTS

The initial experiments were carried out by applying a small negative bias (approximately 300 mV) to the specimen while maintaining a tungsten grid, which was situated a few mm above the surface, at ground potential. The net effect of this procedure was to establish a small acceleration region above the surface. Situated perpendicular to and behind the grid was a grounded stainless steel tube which served as a drift region. Such an arrangement, of course, produced a steradiancy filter. The procedure in the initial experiments consisted of recording the detected low energy electron signal as a function of primary electron energy (E_0). The results are shown in Figure 4. The threshold excitation spectrum consists of three peaks (3.5, 4.5, 6.3 eV). Also shown in Figure 4 are the electron transmission results of Huang and Hamill⁽¹⁵⁾. The agreement between the two is excellent. Huang and Hamill attributed the peaks to optically forbidden excitonic transitions since: (i) the transitions were not observed in light transmission experiments⁽¹⁶⁾, (ii) the transitions were not observed in high energy, small angle electron scattering⁽¹⁷⁾ where dipole selection rules should hold, and (iii) they are observed as resonant electron scattering with electron transmission. The fact that the same structure is observed with TES (with better energy resolution) demonstrates unambiguously that the TES approach is indeed a feasible method of performing surface analysis.

3. PRESENTATIONS AND PUBLICATIONS

The results of this program were presented at the 1984 Molecular Dynamics and Surface Chemistry Conference which was held at the Weapons Laboratory at Kirtland Air Force Base on 24-26 October.

The results of this program are also described in a paper ("Threshold Excitation Spectroscopy of Lithium Fluoride

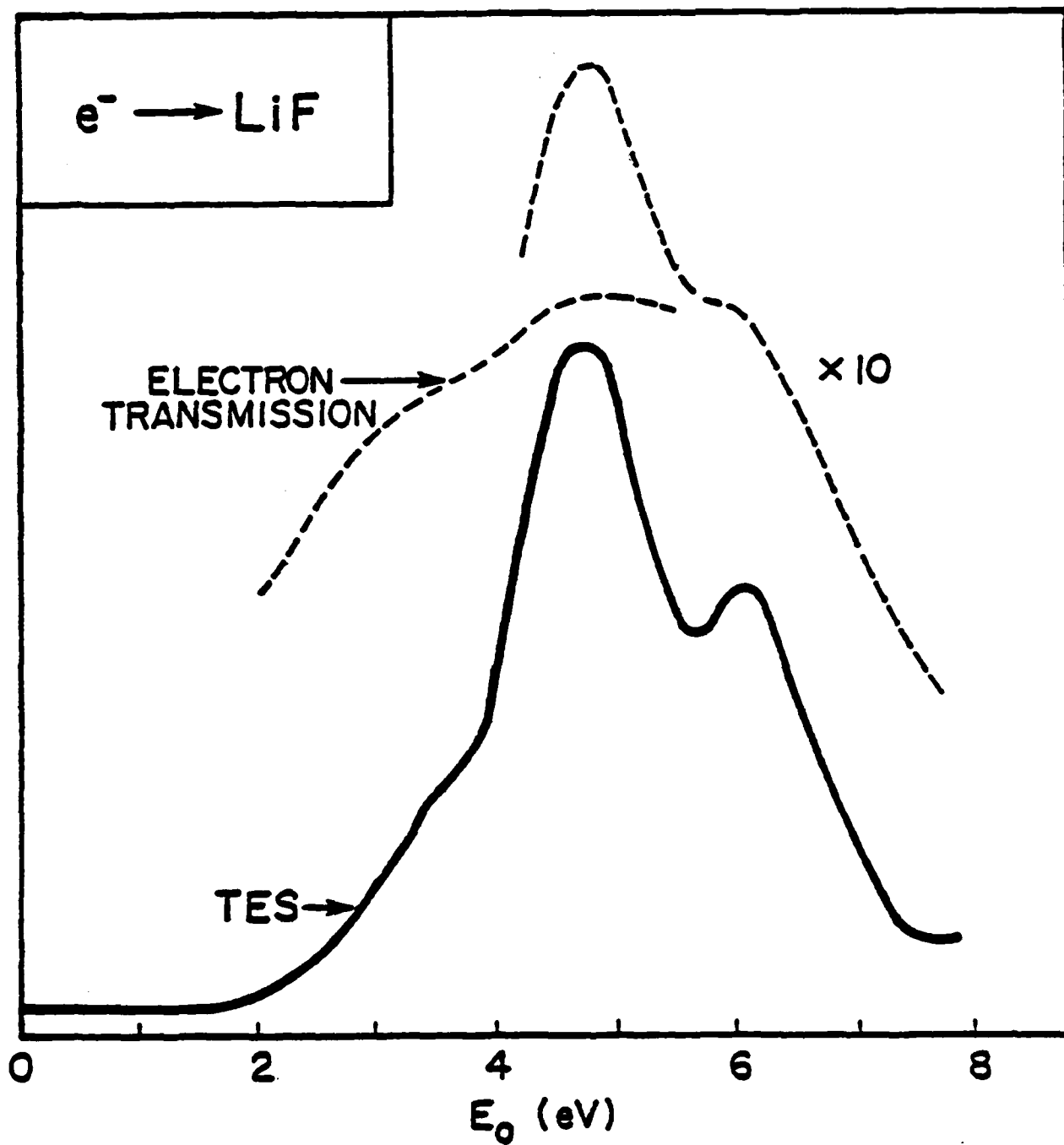


Figure 4. Threshold Excitation Spectrum and Electron Transmission Spectrum (from Reference 15 of LiF.

Surfaces", P. T. Murray) which will be submitted to the Journal of Chemical Physics in the near future.

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